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Novel Gas Phase Ion Molecule Reactions of C_{60}^{++} with O_2

by

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GAS PHASE ION-MOLECULE REACTIONS OF DOUBLY CHARGED FULLERENES WITH OXYGEN

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Abstract

The gas phase ion-molecule chemistry of doubly charged fullerene cations (C_n^{++} where $n=46,48,\dots,60$ & 70) with neutral oxygen molecules, were investigated using a triple quadrupole mass spectrometer. In this paper, we report additions to the fullerene cage structure which result in the formation of C_nO^{++} , $C_nO_2^{++}$, and $C_nO_3^{++}$ product ions from the C_n^{++} reagent ion. In addition, we also report charge transfer reactions resulting in the production of C_n^+ and O_2^+ ions, as well as reactive charge transfer reactions generating C_nO^+ and O_3^+ . All of these processes are a result of low energy ion-molecule collisions ($0.1-24.5$ eV_{lab}). The normalized intensity of the fullerene products exhibit little dependence on size of fullerene clusters examined. However, the reactivities of the fullerenes are found to be highly dependent on the collision energy and the oxygen pressure within the collision cell.

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A) INTRODUCTION

With the discovery of another carbon allotrope, the fullerenes^{1,2}, a new area of research endeavor has been opened. These highly symmetric molecules have attracted much theoretical³⁻⁶ and experimental investigation⁷⁻¹⁰. However, it was the production and isolation of fullerenes in bulk quantities by Huffman and Krätschmer¹¹ that enabled the investigation of these pure carbon clusters to progress rapidly and allowed the chemical reactivity as well as the physical properties to be investigated by numerous methods¹².

A large number of gas phase investigations of fullerenes, mainly involving C_{60} , have been completed enabling a number of physical properties to be determined⁷. Among these properties, the first and second ionization energy (IE) of C_{60} have attracted much interest. The IE of C_{60} has been determined to be 7.61 ± 0.1 eV^{13,14}. Several independent investigations have produced distinctly different results for the IE of C_{60}^+ (i.e. $C_{60}^+ \rightarrow C_{60}^{++} + e^-$), depending on the method of analysis^{13,15-18}. A synchrotron radiation study determined the second IE of C_{60} (i.e. $C_{60} \rightarrow C_{60}^{++} + 2e^-$) to be 19.00 ± 0.03 eV¹⁹. Assuming this second IE of C_{60} to be correct, the IE of C_{60}^+ would be 11.39 ± 0.1 eV. The first IE of various fullerene clusters has been investigated by McElvany and co-workers^{14,20}. They have shown that the fullerenes which are produced in the largest quantities (C_{50} , C_{60} , C_{70}) have the highest IE values^{14,20}.

Investigations of the reactions of fullerenes with oxygen have uncovered numerous surprising results. Fleming and co-workers reported the oxidation of solid C_{60} at 306 °C in a pure oxygen atmosphere^{21,22}.

Investigations by Cox and co-workers of solution phase photo-irradiated fullerenes in an oxygenated benzene solution has resulted in the production and isolation of the first fullerene epoxide²³. Cooks, Ben-Amotz and co-workers reported the additions of O, CH₂, CH₃, and OH to C₆₀ and C₇₀²⁴ using negative chemical ionization. Miller and Chen²⁵ have reported the detection of H⁺, O⁺, OH⁺, H⁻, and OH⁻ additions to C₆₀ and C₇₀ in the fast-atom bombardment mass spectra of pure fullerenes (C₆₀, and C₇₀ only). Collision induced dissociation (CID) studies of these fullerene species suggested that the oxygen atoms are attached to the external surface of the fullerenes²⁵.

Gas phase investigations involving (8 KeV) collisions of singly charged fullerenes cations (C₆₀⁺) with oxygen did not show any associative reactions¹⁵. The product ions include doubly charged carbon clusters resulting from charge-stripping, as well as singly charged ions resulting from CID. Investigation of high energy collisions (4 KeV) of C₆₀⁺⁺ with oxygen resulted in : 1) charge stripping, with C₆₀³⁺ detected; 2) an electron capture, with C₆₀⁺ detected; and 3) the observation of singly and doubly charged fullerenes of smaller cluster size, resulting from CID processes²⁶.

In this paper, we report the first gas phase addition of oxygen to the cage structure of neat fullerenes ions. The reported additions occurred for all doubly charged fullerenes investigated. The fullerenes investigated ranged in cluster size from C₄₆ to C₆₀ and C₇₀. The low energy (1-25 eV_{lab}) gas phase collisions of these doubly charged fullerene cations with oxygen in the collision region of a triple quadrupole mass spectrometer result in the production of C_nO⁺⁺, C_nO₂⁺⁺, C_nO₃⁺⁺, C_n⁺, and C_nO⁺. We pro-

pose that the addition of oxygen to the fullerene cations result in the production of the same species (e.g. same functional group addition) independent of cluster size.

B) EXPERIMENTAL

All studies conducted in this investigation were performed on a VG TRIO-3 Triple Quadrupole Mass Spectrometer. The experimental procedure and instruments of this type have been described previously ^{27,28}. Briefly, the experimental setup consists of three quadrupoles in a tandem geometry. The first quadrupole (Q1) acts as a mass filter for the fullerene ions produced in the electron impact (100 eV) ionization source. The second quadrupole acts as a RF only ion guide (q2) and contains a neutral gas cell (0.1-10 mTorr). The third quadrupole mass filter (Q3) is scanned to analyze any product ions exiting q2. The translational energy of the mass selected ions was varied such that the initial ion-molecule collision can occur in the range of 0.1-200 eV lab frame.

The fullerenes employed in the study were purchased from the Texas Fullerene Corporation as fullerene enriched soot and extracted with toluene¹¹. The oxygen used was 99.0% pure (Airco) as determined by mass spectrometry.

C) RESULTS and DISCUSSION

All the reported reactions below appear to be independent of source and probe temperature.

1) Reactions of C_n^+

Singly charged fullerenes appear to show no reactivity with oxygen at these experimental conditions. The only ions detected in Q3 corresponded to the unreacted singly charged fullerenes passing through the collision region.

2) Reactions of C_n^{++}

(i) Cluster Size Dependence

The passage of different doubly charged fullerene cations (C_n^{++} ; $n=46,48,\dots,60$ & 70) through O_2 produced the same product ions for each of the fullerenes investigated. The ions observed correspond to: C_nO^{++} , $C_nO_2^{++}$, $C_nO_3^{++}$, C_n^+ , C_nO^+ , O_2^+ , O_3^+ , as well as unreacted C_n^{++} (Figure 1).

All fullerene ions investigated reacted with oxygen independent of the fullerene cluster size. That is, at the same initial center of mass collision energy^{29a} and pressure, the percent total ion current^{29b} of the fullerene cations appears to be constant and is shown in Figure 2 and is consistent with the expected similarities in structure for the fullerenes studied³⁰. We speculate that the C_nO^+ ion produced is an epoxide, similar to that reported by Cox *et al.*²³ and Ben-Amotz *et al.*²⁴.

(ii) Energy Dependence

The dependence of product ion abundance on the kinetic energy of the doubly charged fullerene reagent is shown in figure 3. An inverse relationship of collision energy to product ion intensity exists. The abundance of the unreacted doubly charged reagent ion clearly increases with increasing collision energy. The low center of mass collision energy^{29a} and the inverse relation to collision energy supports the conclusion that we are observing an exothermic reaction with little or no activation barrier^{31,32}. At a lab frame collision energy greater than 12.5 eV the species C_{60}^+ and $C_{60}O^+$ are not detected and at collision energies greater than 24.5 eV_{lab} the species $C_{60}O^{++}$ and $C_{60}O_2^{++}$ are not detected. For all collisions at initial collision energies greater than 24.5 eV_{lab} we did not detect any product ions. The ion-molecule interactions at energies greater 24.5 eV_{lab} may produce reaction intermediates too rich in internal energy to be stabilized by successive collisions. As a result, the reaction intermediates decompose into C_{60}^{++} and O_2 , the original reactants.

It has been proposed by Bohme and co-workers^{17,33,34} that the associative complexes observed in Selective Ion Flow Tube (SIFT) experiments for C_{60}^{++} , and C_{70}^{++} with neutral molecules are a result of an ion-induced dipole interaction³⁴. The experiments performed here are similar to the experiments in SIFT tubes. We note that the major differences are:

- 1) the mass selected fullerene ions are "thermalized" prior to reaction, via successive collisions with an inert gas (He) in the SIFT experiment.
- 2) the number of bimolecular fullerene ion and neutral reagent collisions are far greater in a SIFT experiment due to the higher pressures and longer

interaction times.

3) A carrier gas (He) is introduced which can collisionally stabilize reaction products in a SIFT experiment.

Bohme propose a model such that localized charges are present on opposite sides of the fullerene dication. The addition of the neutral to the C_n^{++} dication increases the distance of charge separation therefore resulting in favorable "coulombic relaxation". This relaxation produces a potential energy well (i.e., the stronger the ion-dipole interaction, the deeper the potential energy well). Bohme's potential energy surface^{17,3-3,34} also suggests an activation barrier resulting from coulombic repulsion between the two monocations produced³⁴. Although there are other factors affecting the efficiency of associative behavior versus charge transfer (such as neutral size³⁴), the existence of an activation barrier suggest a direct dependence on collision energy for the relative abundance of charge transfer versus associative behavior. It should be noted that in Bohme's SIFT experiments no reactivity was observed for C_{60}^{++} with O_2 ¹⁷.

The reactions of doubly charged fullerenes with O_2 reported here may be a result of the fullerenes cations having a broad distribution of internal energies and therefore can not be accounted for in Bohme's ground state potential energy diagram. Our data presented here reflects the chemistry of "unthermalized" fullerenes and cannot be applied directly to the chemistry of ground state fullerenes. A recent study of the multiphoton excitation of C_{60} but Wurz *et al.* revealed that fullerenes are capable of internal energies on the order of 50 eV³⁵. It is then possible that the fullerene cations, which we observe to be reactive, possess large internal

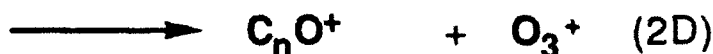
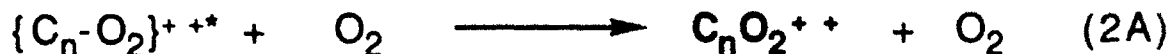
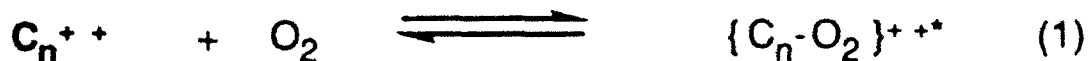
energies. The inertness observed for C_{60}^{++} in SIFT experiments by Bohme and co-workers¹⁷ reflects the chemistry of thermalized fullerenes. Therefore, the observed charge transfer reactions we report here, we feel, are due primarily to a vibrationally excited C_n^{++} reagent, produced via electron impact.

The energy dependence of the reaction observed here supports a coordinate diagram for an exothermic process with little or no activation barrier^{31,32}. Additional investigations are required for a more detailed understanding of the potential energy surface involved in these systems.

(iii) Pressure Dependence

The dependence on reactivity as a function of oxygen pressure is shown in Figure 4. A direct relationship of pressure to product ion intensity exists such that the abundance of unreacted doubly charged cations decreases steadily as the oxygen pressure is increased. At high pressure (10 mTorr O_2) $C_{60}O^+$ is the most abundant product ion, while at the lowest pressures, (1.4-1.6 mTorr O_2), the abundance of $C_{60}O^{++}$ and $C_{60}O_2^{++}$ are almost identical. At pressures below 1.4 mTorr the product ion abundances are too low to be measured accurately. As the number of bimolecular collisions increases, the likelihood of collisionally stabilizing an activated complex ($C_n-O_2^{++*}$) also increases³⁶. However, when the ion-molecule collisions become too energetic, the activated complex ($C_n-O_2^{++*}$) undergoes unimolecular decomposition which results in only the original reactants being detected.

We propose a mechanism for the observed reactions as follows:



where $n=46,48,\dots,60$ & 70 .

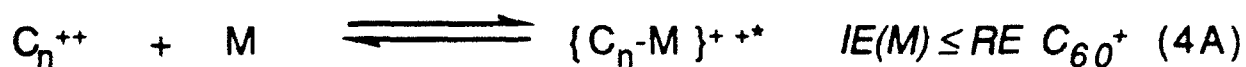
The boldface cations are the product ions which are directly detected in the third quadrupole of the tandem mass spectrometer. The unstable adduct, $\{\mathbf{C_n-O_2}\}^{++}$, is expected to be the activated complex resulting from the interaction of the doubly charged fullerene and the neutral oxygen (rxn 1). The activated complex may require collisional stabilization^{36,37} by a second O_2 (rxn 2A). A second mechanism of stabilization, photoemission^{36,37} can not be disregarded. In addition to detecting O_2^+ , and O_3^+ a small amount of O_4^+ was observed. Indeed it would be naive to suggest this mechanism as the only pathway to the observed product ions. There may well be numerous other pathways to each of the product ions detected, however, we expect such mechanism to be playing minor roles.

The passage of doubly charged fullerenes (C_{60}^{++}) through other target gases (He, Ar, N_2 , CH_4) at similar collision energies ($0.1\text{-}200 \text{ eV}_{\text{lab}}$) did not result in the observation of any associative reactions. We have observed that NH_3 ³⁸, O_2 and a variety of other molecules with IE's ≤ 12.0

exhibits this type of reactivity. A direct correlation exists between reactivity and the IE of the target molecule. The first IE's of He, Ar, N₂, CH₄, O₂, and NH₃ are 24.6³⁹, 15.7³⁹, 15.5⁴⁰, 12.6⁴⁰, 12.0⁴⁰, 10.2⁴⁰ eV respectively. The IE of C₆₀⁺ has been determined to be 11.39 ± 0.1 eV¹⁹.

We anticipate that the reactions observed for oxygen will occur for other molecules if:

- 1) the recombination energy (RE) of C₆₀⁺⁺ is greater than the IE of the neutral, and
- 2) other factors (such as steric hindrance) do not play a predominate role in the formation and stabilization of the ion-molecule complex. A generalized mechanism for this family of ion-molecule processes is illustrated below in reaction 4 .



The inertness of single charged C₆₀ may be a result of its low recombination energy^{21,41} 7.6 eV^{13,14}. We anticipate that only molecules with an IE less than 7.6 eV will be reactive towards singly charged fullerenes.

D) CONCLUSIONS

We have observed addition, charge transfer, and reactive charge transfer reactions for C_n^{++} with O_2 which do not occur for the singly charged fullerenes. We believe this to be part of a general family of charge exchange reactions for unthermalized doubly charged fullerenes, produced via electron impact. We postulate that these ion-molecule reactions will occur for other gases whose IE falls below the recombination energy of the doubly charged fullerenes. Our group is now involved in an ongoing program to examine this reactivity for a variety of chemical systems.

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- 29a) Due to the multiple collision conditions employed in this study, the center of mass frame of reference is valid only for the initial collision. We have no information as to the center of mass collision energy or the lab frame collision energy after the initial collision has occurred. We do not expect the product ions to be a result of singly collision conditions, but to reflect the internal energy of the collision complex. The collision complex may be formed on the initial collision or by successive collision.
- 29b) The percent total ion current was determined as follows $PTIC = \{X_a / (X_a + X_b + X_c + \dots)\} * 100$ where X_a, X_b, X_c, \dots are the ion currents resulting from each species a, b, c, ... detected. Data is presented in this manner to account for differences in abundance for each fullerene cation.
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- 42) The $^{12}\text{C}:^{13}\text{C}$ isotopic ratio does not indicate a 1 m/z addition for any product ions or for unreacted C_{60}^{++} with exception of C_{60}^+ . We expect the enlarged 721 amu peak to be a result of a minor hydrogen contaminate present in the collision cell. No indication of hydrogen contaminate was present in any other detected ions. Additional experiments were performed with D_2O , and the product ions detected are at a different mass to charge ratio from the ions reported here (i.e. $\text{C}_{60}\text{D}_2\text{O}^{++}$,). This work will be reported explicitly elsewhere.

FIGURE CAPTIONS

FIGURE 1) Averaged mass spectra recorded after C_{60}^{++} is collided with O_2 at 2 eV_{lab} and 8.5 mTorr of oxygen⁴².

FIGURES 2 A & B) Relative product ion intensities for fullerenes C_{46} through C_{70} at 8.5 mtorr of oxygen and 0.17 eV_{cm} ^{29a}. The lab frame collision energy was adjusted such that the first collision of each fullerene fraction would have the same center of mass collision energy. The source temperature is 300°C and probe temperature 620°C .

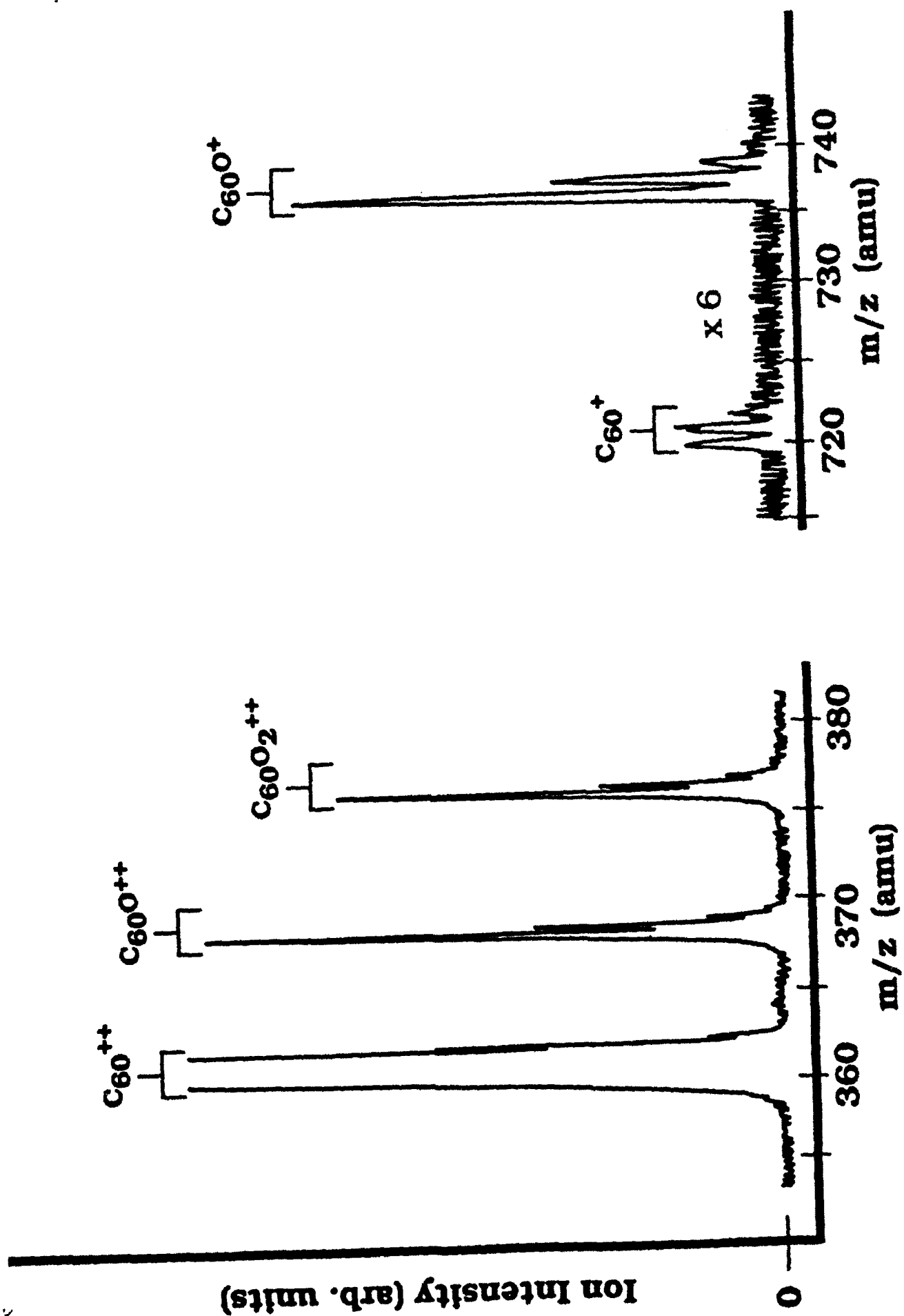
KEY a) $\square C_n^{++}$ ΔC_nO^{++} $\circ C_nO_2^{++}$
 KEY b) $\blacktriangle C_n^+$ $\bullet C_nO^+$

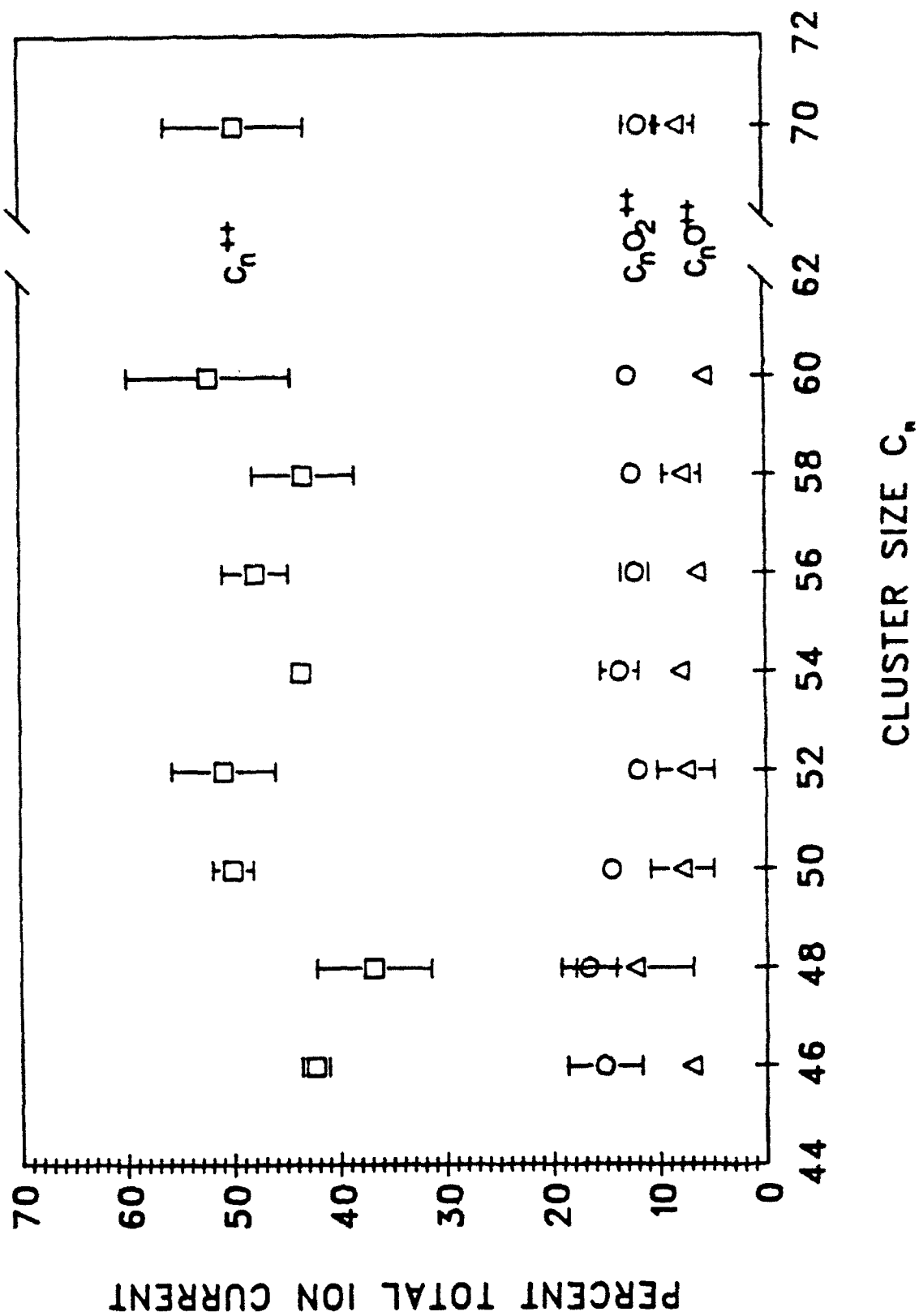
FIGURE 3 A & B) Collision energy dependence for reported reactions. The collision cell pressure of 8.5 mTorr of oxygen, source temperature 300°C , probe temperature 620°C .

KEY a) $\square C_{60}^{++}$ $\blacklozenge C_{60}O_2^{++}$ $\blacksquare C_{60}O^+$
 KEY b) $\Delta C_{60}O^{++}$ $\blacklozenge C_{60}O_2^{++}$ $\blacktriangle C_{60}O_3^{++}$ $\times C_{60}^+$

FIGURE 4 A & B) Pressure dependence for reported reactions of C_{60}^{++} and O_2 . Collision energy of 5 eV_{lab} , source temperature 300°C , probe temperature 620°C .

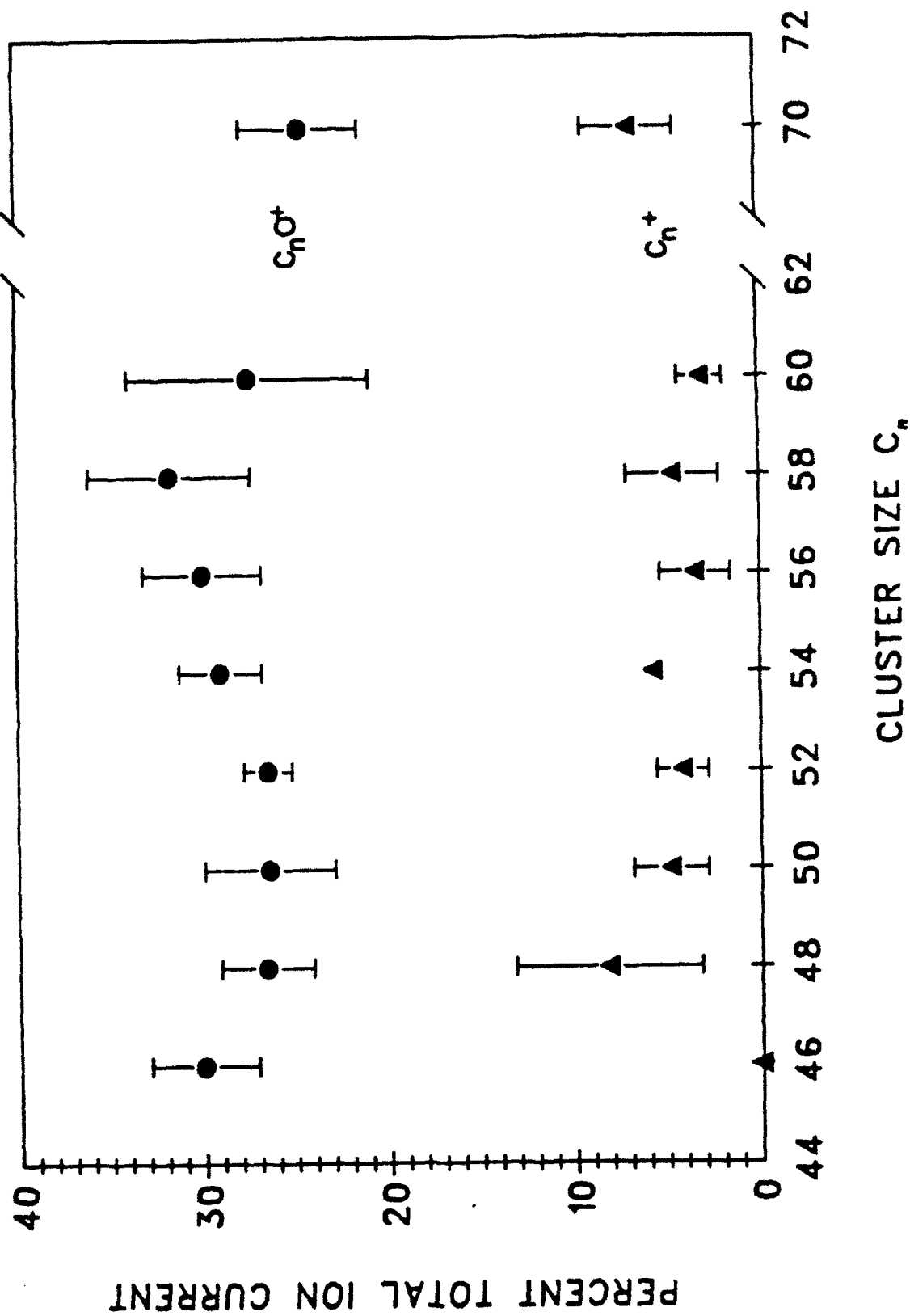
KEY a) $\square C_{60}^{++}$ $\blacklozenge C_{60}O_2^{++}$ $\blacksquare C_{60}O^+$
 KEY b) $\Delta C_{60}O^{++}$ $\blacklozenge C_{60}O_2^{++}$ $\blacktriangle C_{60}O_3^{++}$ $\times C_{60}^+$





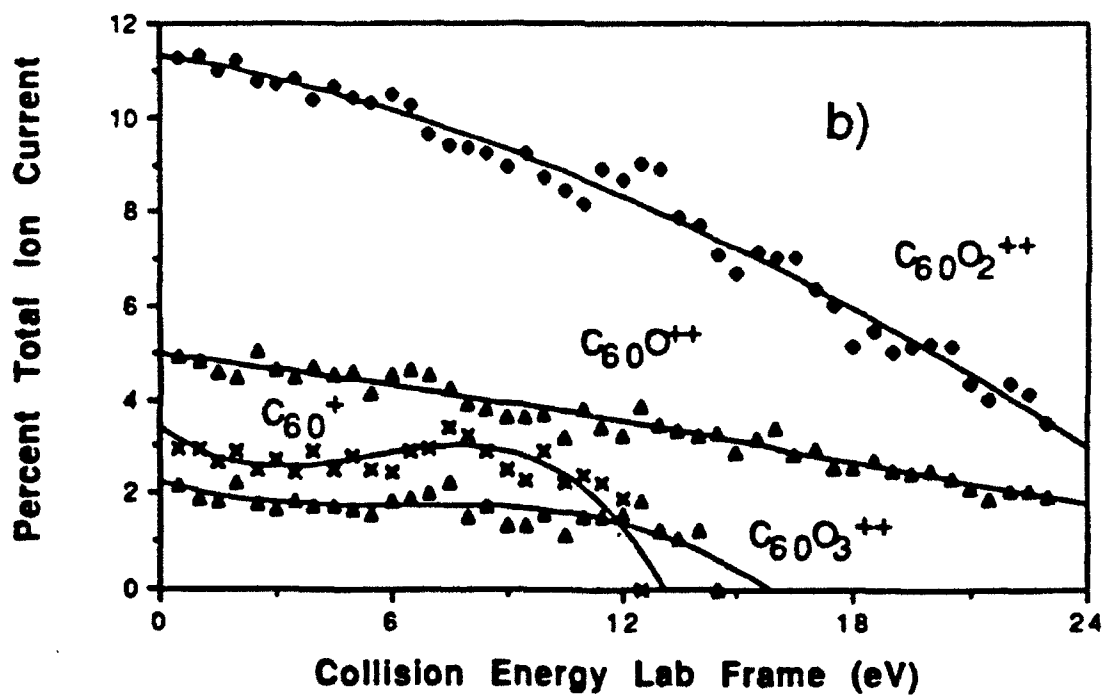
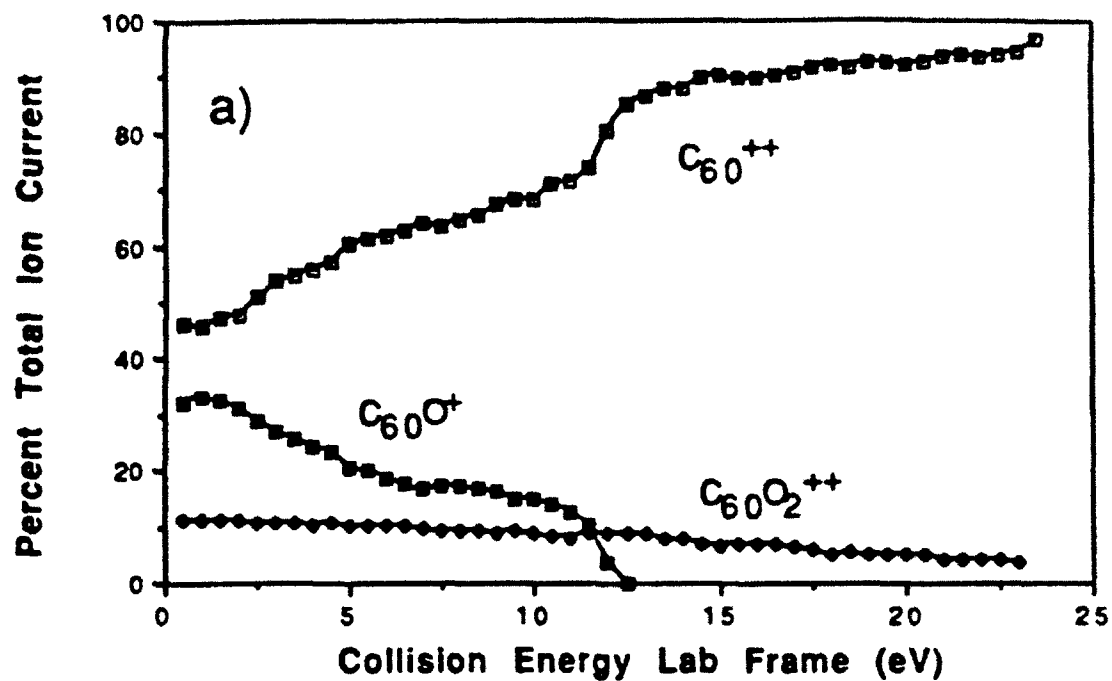
SEE FIGURE 2A

LOWRY & GARDNER



5: STAY & GARDNER

FIGURE 2b



STAY & GAMMA
FIG. 3

